The geminal basis in explicitly correlated wave functions

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ABSTRACT

In 1985 Kutzelnigg showed that a large percentage of the electron correlation energy for helium can be recovered using a single explicitly correlated basis function, chosen to fit the cusp at the correlation hole. In particular the simple wave function $\Psi = (1 + \frac{1}{2}r_{12})\Phi$ returned more than 80% of the correlation energy. In this paper we return to Kutzelnigg's simple ansatz and remove the conventional double excitations in explicitly correlated CC2 theory (denoted as CCS(F12)), applying all established developments in modern F12 theory, such as replacing linear r_{12} with $f(r_{12}) = \exp(-\gamma r_{12})$ and the use of auxiliary basis sets for the standard RI approximation in R12 theory. Analysing different approximations we show that in general the CCS(F12) approach yields 80–95% of the CC2 correlation energy, which is astonishingly large considering the small number and restricted form of the geminal basis functions.

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1. Introduction

In 1985 Kutzelnigg published his landmark paper "r_{12}-Dependent terms in the wave function as closed sums of partial wave amplitudes for large l" [1]. Through his lucid analysis for helium Kutzelnigg understood that a large percentage of the electron correlation energy can be recovered from a single term, linear in r_{12}, the interelectronic separation, chosen to fit the cusp at the bottom of the correlation hole [2–4]. Kutzelnigg performed calculations on the ground state of helium at the levels of second order perturbation theory using the $1/Z$-expansion and configuration interaction (CI) theory. He found that the simple wave function expansion

$$\Psi = (1 + \frac{1}{2}r_{12})\Phi, \tag{1}$$

$$\Phi = e^{-\zeta(r_1+r_2)}[\alpha\beta - \beta\alpha], \tag{2}$$

returned more than 80% of the correlation energy (here defined as $E_{\text{exact}} - \langle \Phi \mid \hat{H} \mid \Phi \rangle$). The optimised exponent ζ for the orbital remained close to that of the bare nuclear Hamiltonian (BN). He proceeded to expand the wave function as

$$\Psi = (1 + \frac{1}{2}r_{12})\Phi + \chi \tag{3}$$

using a partial wave expansion for χ and found that for second order perturbation theory the energy increments $E_l^{(2)}$ go asymptotically as l^{-8}, in contrast to l^{-4} for conventional partial wave expansions where the $\frac{1}{2}r_{12}\Phi$ term is absent. This remarkable acceleration in the rate of convergence was shown to result directly from

the explicit representation of the linear r_{12} nature of the correlation cusp, for which the partial wave expansion in conventional calculations converges extremely slowly. The generalisation of these ideas to many-electron systems followed quickly. For example, in the MP2-R12 method the first order pair functions $|\mu_{ij}\rangle$, the response of the Hartree–Fock orbital pair $|\phi_i\phi_j\rangle$ to the introduction of correlation, are expanded as

$$\mid \mu_{ij} \rangle = \sum_{k \leqslant l} c_{ij}^{kl} \hat{Q}_{12} r_{12} \mid \phi_k\phi_l \rangle + \sum_{a \leqslant b} t_{ij}^{ab} \mid \phi_a\phi_b \rangle. \tag{4}$$

In addition to the conventional expansion in virtual orbital pairs $|\phi_a\phi_b\rangle$, a small set of geminal basis functions $\hat{Q}_{12}r_{12} \mid \phi_k\phi_l \rangle$ is used, where $\phi_k\phi_l$ are occupied Hartree–Fock orbitals. $\hat{Q}_{12}$ is the strong orthogonality projector that ensures that the usual Slater–Condon rules apply to the geminal basis. The coefficients c_{ij}^{kl} can either be optimised or fixed according to the cusp conditions (in a spin-adapted basis $c_{ij}^{ij} = \frac{1}{2}$ or $\frac{1}{4}$ for singlet and triplet pairs, respectively, all other terms $c_{ij}^{kl} = 0$). First MP2-R12 calculations for molecules were reported in 1987 [5] and pilot CI-R12 calculations were published in 1991 [6]. By 1995, integral direct CCSD(T)-R12 calculations were possible [7]. Recently, many new developments in R12 theory have appeared such as the introduction of a dedicated auxiliary basis for Kutzelnigg's resolution of the identity method for the efficient evaluation of many-electron integrals [8], density fitting approximations for the efficient evaluation of the various two-electron integrals [9], and general functions of r_{12} instead of linear r_{12} [10]. These advances, particularly the replacement of r_{12} with $f(r_{12}) = (1 - e^{-\gamma r_{12}})/\gamma = r_{12} + \mathcal{O}(r_{12}^2)$, have paved the way for highly efficient explicitly correlated coupled-cluster methods that return chemical accuracy using only triple-ζ quality basis sets [11–17]. It is, however, remarkable that Kutzelnigg's paper in 1985

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still embodies all the ideas central to modern R12 theory. In this article we return to the pioneering work of Kutzelnigg and ask the question "How well does the ansatz $(1 + \frac{1}{2}f(r_{12}))\Phi_{HF}$ perform when generalised to molecules?"

There is clearly a huge redundancy between the terms $\frac{1}{2}f(r_{12})\Phi_{HF}$ and χ and it should be possible to exploit this redundancy to further improve upon the current R12 methods. We are particularly interested to investigate the sensitivity of this ansatz on the function $f(r_{12})$. These questions are additionally motivated by a comparison of R12 theory with GGn theories [18–21], where the first order pair functions are expanded as

$$| \mu_{ij}\rangle = \sum_{p \leqslant q} \sum_{v} c_{ij}^{pq,v} f_v(r_{12}) | \phi_p \phi_q\rangle, \tag{5}$$

which includes the conventional expansion if the set of $f_v(r_{12})$ includes $f_v(r_{12}) = 1$. According to Kutzelnigg's analysis, this expansion should also be dominated by just a few geminal terms, those that are common to both the GGn and the R12 expansions. In GGn calculations, however, this is not evident due to the use of the weak orthogonality functional.

This article is organised as follows: In Section 2 we repeat Kutzelnigg's CI calculations for the ground state of helium, replacing linear r_{12} with $(1 - e^{-\gamma r_{12}})/\gamma$. In Sections 3–5 we present coupled-cluster calculations for molecules using only the explicitly correlated geminal basis to expand the pair excitations.

2. CI-R12 calculations on parahelium

Before turning to molecules, it is instructive first to revisit Kutzelnigg's original calculations on helium. Here we report variational calculations on the ground state of parahelium using wave functions of the form

$$\Psi = (1 + c\,f(r_{12}))\Phi, \tag{6}$$

$$\Phi = \phi(r_1)\phi(r_2)\frac{1}{\sqrt{2}}[\alpha\beta - \beta\alpha], \tag{7}$$

$$\phi = \sum_{i=0}^{n} C_i r^i e^{-\zeta r}. \tag{8}$$

Kutzelnigg presented calculations choosing $c\,f(r_{12}) = \frac{1}{2}r_{12}$ and $\phi = e^{-\zeta r}$ (i.e. $n = 0$). ζ was chosen to correspond to either the bare nuclear orbital ($\zeta = 2$), or optimised to give the best reference Φ or the best function $(1 + \frac{1}{2}r_{12})\Phi$. We are interested in how sensitive his conclusions are to the correlation factor $c\,f(r_{12})$ and to the reference Φ. We present results for three functions $f(r_{12})$, namely r_{12}, $(1 - e^{-r_{12}})$ and $(1 - e^{-\gamma r_{12}})/\gamma$, with γ variationally determined and the coefficient c is chosen to either be $\frac{1}{2}$, or to be variationally optimised.

We also investigate two choices of ϕ, the bare nuclear orbital or the HF orbital.

In Table 1 we present the energies of the 12 wave functions of the form $(1 + c\,f(r_{12}))\Phi$. $E_{ref} = \langle\Phi | \hat{H} | \Phi\rangle$, E_{corr} denotes the correlation energy $E - E_{ref}$ and the error is defined as $E_{exact} - E$. The energies E_{corr} correspond to what Kutzelnigg called the overhead for an R12 calculation. From our calculations we see that combining $\frac{1}{2}r_{12}$

with the HF reference for Φ results in a poor wave function. This is because the correlation factor r_{12} acts to expand the wave function, spoiling the approximately correct extent of Φ_{HF}. If one reduces the coefficient from 0.50 to 0.16, the error is halved. Alternatively, shrinking the orbital to that of the bare nucleus also halves the error.

The situation for the exponential correlation factor is somewhat different. In combination with the bare nucleus reference, $(1 + \frac{1}{2}(1 - e^{-r_{12}}))$ gives a relatively poor correlation energy. By virtue of the exponential decay, this correlation factor does not expand the wave function to the same extent as linear r_{12} and the wave function is too contracted. However, the wave function $(1 + \frac{1}{2}(1 - e^{-r_{12}}))\Phi_{HF}$ represents a significant improvement over the original choice of $(1 + \frac{1}{2}r_{12})\Phi_{BN}$, reducing the error by 25%. The best correlation energy is obtained by using the HF reference with the exponential correlation factor and optimising c and γ, but these parameters remain close to $\frac{1}{2}$ and 1, respectively. Finally, we note that this wave function recovers 64% of the correlation energy (defined as $E - E_{ref}$). Although this value is much less than the 80% reported by Kutzelnigg, this apparent discrepancy only arises due to the differing E_{ref} that are used to define the correlation energy. Using the definition $E - E_{HF}$, the wave function $(1 + \frac{1}{2}r_{12})\Phi_{BN}$ recovers only 35% of the correlation energy. Seen in this light, the 64% obtained by F12 is an impressive improvement.

3. Explicitly correlated coupled-cluster theory

To generalise Kutzelnigg's simple ansatz for molecules we adopt the framework of explicitly correlated coupled-cluster theory. In the normal explicitly correlated ansatz the conventional wave function expansion is augmented with additional R12 double excitations. The new excitations are intended to improve the wave function predominantly in the short range region around the electron–electron cusp, while the conventional excitations are kept to describe the overall wave function. Here, we discard the conventional double excitations, using only the explicitly correlated geminal basis to expand the doubles. The single excitations are expanded using virtual orbitals in the usual way. Our selected coupled-cluster model is CC2 [22].

3.1. The CCS(F12) model

The CCS(F12) model is analogous to the CC2 model but the conventional double excitations are replaced with R12 double excitations. The CCS(F12) wave function is

$$| CC\rangle = \exp(\hat{T}) | HF\rangle, \tag{9}$$

where the reference state is the Hartree–Fock wave function and

$$\hat{T} = \hat{T}_1 + \hat{T}_{2'}. \tag{10}$$

For a closed-shell reference state the excitation operators are:

$$\hat{T}_1 = \sum_{ai} t_i^a E_{ai}, \tag{11}$$

Table 1
Energies of parahelium ($-\mu E_h$) from wave functions of the form $(1 + c\,f_{12})\Phi$.

Φ	E_{ref}	c	r_{12}		$1 - e^{-r_{12}}$		$(1 - e^{-\gamma r_{12}})/\gamma$	
			E_{corr}	Error	E_{corr}	Error	E_{corr}	Error
BN	2,750,000.0	$\frac{1}{2}$	126,582.3	27,142.1	98,904.1	54,820.3	117,112.5	36,611.9
		opt	127,125.1	26,599.2	100,134.6	53,589.8	129,310.3	24,414.1
HF	2,861,680.0	$\frac{1}{2}$	−12,678.2	54,722.6	22,023.7	20,020.8	26,016.4	16,028.0
		opt	18,938.5	23,105.9	27,028.5	15,015.9	27,061.8	14,982.6

E_{exact} = 2,903,724.4.

$$\hat{T}_{2'} = \sum_{\alpha\beta ij} t_{ij}^{\alpha\beta} E_{\alpha i} E_{\beta j}. \tag{12}$$

We have used the usual convention that $i,j,\ldots$ denote occupied and $a,b,\ldots$ unoccupied (virtual) orbitals. The indices $\alpha,\beta,\ldots$ are used to denote orbitals of a complementary subspace (*vide infra*). The CCS(F12) equations are:

$$E = \langle \mathrm{HF}|\hat{H}(1 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_{2'})|\mathrm{HF}\rangle, \tag{13}$$

$$0 = \langle \mu_1 | \tilde{F} + \tilde{\phi} + [\tilde{\phi}, \hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{14}$$

$$0 = \langle \mu_{2'} | [\hat{F}, \hat{T}_{2'}] + \tilde{\phi}|\mathrm{HF}\rangle, \tag{15}$$

with the usual definitions for the projection manifolds [23–25]. $\hat{F}$ refers to the Fock-operator, $\hat{H}$ the Hamiltonian and $\hat{\phi}$ the fluctuation potential:

$$\hat{H} = \hat{F} + \hat{\phi}. \tag{16}$$

The tilde indicates $\hat{T}_1$-transformed quantities

$$\tilde{A} = e^{-\hat{T}_1}\hat{A}e^{\hat{T}_1}. \tag{17}$$

In Eq. (15) the Fock operator is not $\hat{T}_1$-transformed because the generalised Brillouin condition (GBC) is applied [26]. The CCS(F12) ansatz should be compared to the CC2 equations which are entirely identical except that $\hat{T}_{2'}$ is replaced by $\hat{T}_2$.

3.2. The explicitly correlated pairs

The operator $\hat{T}_{2'}$ contains a particular form of double excitations, which are denoted R12 excitations. The detailed properties of these excitations are:

$$t_{ij}^{\alpha\beta} = \sum_{kl} c_{ij}^{kl} w_{kl}^{\alpha\beta}, \tag{18}$$

$$w_{kl}^{\alpha\beta} = \langle \phi_\alpha \phi_\beta | \hat{Q}_{12} f(r_{12})|\phi_k \phi_l \rangle. \tag{19}$$

The c_{ij}^{kl} are the R12 amplitudes that are to be determined. $\hat{Q}_{12}$ ensures that the new excitations are strongly orthogonal on the Hartree–Fock reference state [27].

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2). \tag{20}$$

This is known as ansatz 2 in R12 theory [8]. When both conventional doubles and R12 excitations are present, as for example in CC2-F12 [23], it is preferable to also project out the virtual pairs [24,28] (see also Refs. [29,30]):

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2). \tag{21}$$

$\hat{O} = \sum_k |k\rangle\langle k|$ is the projection operator onto the occupied Hartree–Fock spin orbitals, $\hat{V} = \sum_a |a\rangle\langle a|$ is the projection operator onto the virtual orbitals. Since no conventional doubles are present in CCS(F12), Eq. (20) is used.

Slater-type geminals (STGs), where $f(r_{12}) = \exp(-\gamma r_{12})$, were introduced into R12 perturbation theory by Ten-no in 2004 [10], and various authors have implemented these functions and assessed their performance [31–40], not only at the level of MP2 theory but also at the coupled-cluster level [11–17], or in multireference perturbation theory [41]. As a general rule, at least quintuple-ζ quality results are obtained in a triple-ζ basis when using STGs (*vide supra*). In the present work, we use STG-nG contracted two-electron Gaussian basis functions with the coefficients and exponents taken from Ref. [33]:

$$f(r_{12}) = \sum_{i=1}^{n} c_i \exp(-\omega_i r_{12}^2) \approx \exp(-\gamma r_{12}). \tag{22}$$

Other correlation factors have also been investigated [33], e.g.

$$f(r_{12}) = r_{12}, \tag{23}$$

$$f(r_{12}) = r_{12}e^{-\gamma r_{12}}, \tag{24}$$

$$f(r_{12}) = r_{12}\mathrm{erfc}(\gamma r_{12}). \tag{25}$$

In our work we will re-investigate the different choices because in the absence of the conventional double excitations the explicitly correlated double excitations have to describe not only the short range region around the cusp but have to provide also the long-range behaviour.

Having decided on the form of $f(r_{12})$, the F12 amplitudes have to be determined. In the literature different possibilities are known. In the framework of the variationally optimised method (*varopt*), a full optimisation of all R12 amplitudes c_{ij}^{kl} is performed, as proposed in Ref. [42]. This method is invariant with respect to rotations among the occupied orbitals. The same holds true when restricting the (spin-adapted) amplitude matrices to the diagonal excitations c_{ij}^{ij} and determining the amplitudes by the rational-generator approach of Ten-no, (*fixed*) [43], which was formulated for coupled-cluster theory in Ref. [12]. In this work we compare both options since the *fixed* approach does not suffer from a geminal basis-set superposition error [35].

4. Computational details

In this work we perform CC2, CC2-F12 and CCS(F12) calculations on a test set of small molecules. The molecules and structures used are summarised in Table 2. All calculations were performed with the frozen core approximation. Hence, we have used the aug-cc-pVXZ basis sets of Dunning and co-workers [44,45], denoted as aVXZ. All explicitly correlated calculations were performed using standard approximation B and a dedicated complementary auxiliary basis set (CABS) [28]. If not otherwise indicated the correlation factor used was a Slater-type geminal expressed in six Gaussian-type geminals (STG-6G) [33]. When basis sets of triple-ζ quality and larger are used for F12 calculations, the influence of CABS is rather small. Even using aVDZ orbital basis as CABS gives correlation energies that differ from the true value by at most one or two millihartrees. Unless otherwise indicated, we have used the aVDZ CABS for all calculations. In some cases for the *varopt* approach, it was necessary to use a larger CABS due to the occurrence of negative eigenvalues in the Fock matrix elements involving F12 functions.

Table 2
Geometries of the investigated molecules. The molecules C_2H_2 through H_2O_2 are used to test the performance of CCS(F12) with respect to chemical reactions. All distances are provided in Ångstrom, the angles in degrees.

Molecule	Ref.	Dist. 1	Dist. 2	Angle 1	Angle 2
BeH_2	a	1.3348		180.000	
CH_2	b	1.1080		102.064	
HF	a	0.9006			
F_2	b	1.4091			
N_2	b	1.0988			
CO	b	1.1302			
$C_2H_3^+$	c	(class.)			
NO^+	d	1.0941			
BeO	d	1.3685			
C_2	d	1.2675			
O_3	e	1.2720		116.800	
CN^+	d	1.1993			
BN	f	1.2830			
C_2H_2	b	1.2122	1.0617	180.000	
C_2H_4	b	1.3332	1.0810	121.326	117.347
CH_4	b	1.0862			
CO_2	b	1.1703			
H_2	b	0.7374			
H_2O	b	0.9614		104.109	
H_2O_2	b	1.4538	0.9668	99.604	112.553

[a] TURBOMOLE-Testsuite, [b] Ref. [51], [c] Ref. [47], [d] Ref. [50], [e] Ref. [48], [f] Ref. [49].

5. Results and discussion

This section is organised as follows: First the CCS(F12) and CC2 basis set limits are compared, followed by a series of studies investigating the influence of the various parameters in the F12 wave function. We also compare the CCS(F12) and CC2 methods for relative energies.

5.1. Basis set limits of CCS(F12) and CC2

The basis set limits of the CCS(F12) and CC2 methods for the molecules in our test set are given in Table 3. To obtain the CCS(F12) limit we have used the *varopt* formulation in combination with a STG correlation factor and optimised the exponents γ to give the most negative correlation energies. Our investigations revealed that for CCS(F12) the same optimal exponent γ was obtained independent of the size of the basis set (triple- or quadruple-ζ quality). Therefore the exponent γ^{opt} was optimised at the triple-ζ level and was used without re-optimisation in calculations using larger orbital basis sets. The CC2 limits were computed with the CC2-F12 model, using STG-6G with an exponent of $\gamma = 1.3\ a_0^{-1}$, *fixed* amplitudes and the aV5Z orbital basis. It can be seen that the obtained *varopt* CCS(F12) correlation energy amounts to between 80% and 95% of the CC2 limit. This is comparable to the percentage of the basis set limit recovered in conventional calculations using a aVTZ basis, which is typically 90%. For the two electron system H$_2$, 97% of the CC2 limit is recovered. These percentages are astonishingly large, particularly when compared to the 65% computed for helium in Section 2. These results show that Kutzelnigg's simple ansatz performs extremely well for molecules, provided that an optimised non-linear correlation factor $f(r_{12})$ is used.

In Table 3 we also compare CCS(F12) calculations using the aVTZ and aVQZ basis sets. It is clearly seen that the results are almost converged for the triple-ζ orbital basis. Differences between small and large orbital basis sets are mainly based on single excitations and a truncated (i.e. finite) CABS. The reason for this rapid convergence is the choice of the explicitly correlated pairs $Q_{12}f(r_{12})\phi_i\phi_j$ which take into account the occupied orbitals only. Hence, we expect a convergence behaviour similar to that of Hartree–Fock with respect to increasing basis sets, namely "almost" convergency for triple-ζ basis sets. This is indeed observed. However, this geminal basis is far from being complete. Up to 20% of the correlation energy is unaccounted for. The reason for this is also due to the choice of the explicitly correlated pairs. In order to recover the remaining correlation using geminal functions only, one possibility is to extend the geminal basis to cover the complete space the conventional pairs act on. The explicitly correlated pairs then take the form $Q_{12}f(r_{12})\phi_p\phi_q$, where p and q denote both occupied and virtual orbitals. This was introduced earlier to describe excited states [46] as well as in the GGn methods [18–21]. In Ref. [46] test calculations are carried out for ground state energies, but both the use of ansatz 1 and the inclusion of the conventional double excitations did not indicate the need of this extension to ground state theory.

5.2. Variationally optimised vs. fixed amplitudes

Kutzelnigg's original idea was to fix the F12 amplitudes according to the cusp conditions. In this section we compare the CCS(F12) correlation energies computed using the *fixed* and *varopt* formulations, where the amplitudes are optimised. CCS(F12)/aVTZ results for the fixed amplitude method are shown in Table 4 and are also given as a percentage of the CCS(F12)/aVTZ-*varopt* values, which are in Table 3. The exponent γ was optimised for each molecule and both methods independently. In general we found that the differences in the optimised γ's are very small. Although the *varopt* method always performs slightly better than the fixed amplitudes approximation, the latter performs surprisingly well, yielding in almost all cases 92–99% of the *varopt* method. This result is remarkable for two reasons. Firstly, when the amplitudes are held fixed the correlated wave function contains a single variational parameter γ for the double excitations. Secondly, the explicitly correlated pairs are chosen such that the short range r_{12} dependence is described, with relatively little reference to longer-range correlation effects. This is perhaps an indication that long-range correlation, particularly that which cannot be described using a spherically symmetric correlation factor, is poorly represented in both the *fixed* and *varopt* approaches and is the dominant contribution to

Table 3
CCS(F12)/aVTZ and CCS(F12)/aVQZ correlation energies compared to basis set limit CC2 values in mE_h.

Molecule	ΔCCS(F12)				
	γ^{opt}	ΔaVTZ	aVQZ	%[c]	ΔCC2^{Limit}
BeH$_2$	0.50	−64.416	−64.492	95.9	−67.259
CH$_2$	0.55	−142.768	−142.887	91.3	−156.550
HF	0.85	−275.012	−273.981	85.5	−320.518
F$_2$	0.80	−523.508[a]	−523.375[b]	84.6	−618.709
N$_2$	0.60	−370.434[a]	−370.266[b]	86.6	−427.552
CO	0.65	−350.296[a]	−350.172[b]	85.1	−411.414
C$_2$H$_3^+$	0.60	−286.131[a]	−286.405	90.0	−318.298
NO$^+$	0.65	−400.493[a]	−400.279[b]	83.8	−477.653
BeO	0.60	−286.422[a]	−286.382[b]	79.0	−362.346
C$_2$	0.40	−380.353[a]	−380.339[b]	92.4	−411.489
O$_3$	0.65	−756.153[a]	−755.921[b]	82.7	−914.165
CN$^+$	0.40	−379.356[a]	−379.222[b]	79.8	−475.431
BN	0.40	−320.348[a]	−320.210[b]	78.9	−405.844
C$_2$H$_2$	0.55	−315.188	−315.325	90.0	−350.526
C$_2$H$_4$	0.60	−344.859[a]	−344.835[b]	91.8	−375.738
CH$_4$	0.60	−204.839	−205.030	93.1	−220.195
CO$_2$	0.65	−599.295[a]	−599.203[b]	85.3	−702.214
H$_2$	0.50	−33.376	−33.368	97.2	−34.329
H$_2$O	0.75	−263.385	−263.068	86.9	−302.710
H$_2$O$_2$	0.70	−497.592[a]	−497.584[b]	86.3	−576.333

[a] CABS increased to aVQZ.
[b] CABS increased to aVTZ.
[c] $\frac{\Delta CCS(F12)}{\Delta CC2^{Limit}} \times 100$.

Table 4
Optimised CCS(F12) Slater-type geminal exponents γ^{opt} for different molecules using the *fixed* method. The exponent was optimised for the *varopt* and *fix* approaches independently. The resolution of the optimisation was 0.05 a_0^{-1}. The correlation energies are provided in mE_h. Larger CABS have to be used for the *varopt* method if the B matrix of R12 theory has negative eigenvalues.

Molecule	γ^{opt}	ΔCCS(F12)	%[a]
BeH$_2$	0.60	−63.775	99.0
CH$_2$	0.65	−139.938	98.0
HF	0.90	−266.148	96.8
F$_2$	0.90	−495.511	94.7
N$_2$	0.70	−352.884	95.3
CO	0.75	−335.547	95.8
C$_2$H$_3^+$	0.65	−275.538	96.3
NO$^+$	0.70	−379.881	94.9
BeO	0.70	−276.529	96.5
C$_2$	0.65	−283.717	74.6
O$_3$	0.75	−697.165	92.2
CN$^+$	0.50	−357.388	94.2
BN	0.55	−304.870	95.2
C$_2$H$_2$	0.65	−301.215	95.6
C$_2$H$_4$	0.65	−333.212	96.6
CH$_4$	0.65	−199.836	97.6
CO$_2$	0.75	−572.820	95.6
H$_2$	0.65	−33.162	99.4
H$_2$O	0.80	−255.100	96.9
H$_2$O$_2$	0.80	−476.369	95.7

[a] $\frac{CCS(F12)[\gamma^{opt}, fixed]}{CCS(F12)[\gamma^{opt}, varopt]} \times 100$.

the deviation between the basis set limits of the CCS(F12) and CC2 methods.

The only case we have observed where *fixed* performs significantly worse than *varopt* is that of the C_2 molecule, where the *varopt-fixed* discrepancy is 25% (96.636 mE_h). This is also reflected in the optimised STG exponents. Whereas in almost all other cases the optimised γ did not change much when switching from the *varopt* to the *fixed* method, this is not true for the C_2 molecule and the exponent increases dramatically from 0.40 to 0.65 a_0^{-1}. Surprisingly, although a similar situation occurs for the BN molecule the *fixed* description of this molecule is in line with the other molecules.

5.3. γ-dependence

The optimised STG exponent for the *varopt* formulation of CCS(F12) yields an average of 0.7 a_0^{-1}, which is clearly smaller compared to the established STG exponent 1.3 a_0^{-1} in explicitly correlated calculations such as MP2-F12 and CCSD(F12). The geminal basis functions are therefore longer range. In this section we investigate the γ-dependence, i.e. how the correlation energies decrease if γ moves away from the optimum value. The results of CCS(F12)/aVTZ calculations for the molecules HF and C_2 are shown in Figs. 1 and 2, respectively. For the HF molecule the *varopt* method seems to be quite insensitive to a wide range of γ whereas the fixed amplitudes show a strong γ-dependence. For the C_2 molecule both the *varopt* and *fixed* methods show a similar pronounced dependence. Comparing HF with C_2, the fixed amplitudes approach for C_2 shows a less pronounced γ-dependence than HF, but on the other hand the *varopt* results for C_2 are more sensitive to a poorly chosen exponent than HF. In general it is obvious that the results depend more strongly on the exponent γ than in methods that use both explicitly correlated and conventional excitations.

5.4. Influence of the correlation factor

The sensitivity of the CCS(F12) method to the choice of correlation factor is also of interest. In Section 2 we have illustrated that the STG is a significant improvement over linear r_{12} in CI calculations for helium. Here we investigate a number of previously considered alternative correlation factors [33]. Results for CCS(F12)/aVTZ calculations on the molecule HF are collated in Table 5. First we investigated the original R12 ansatz, choosing the correlation factor to be linear in the interelectronic distance $f(r_{12}) = r_{12}$. Just as for the CI calculations on the helium atom, this approach performs fairly poorly for molecules in the framework of CCS(F12).
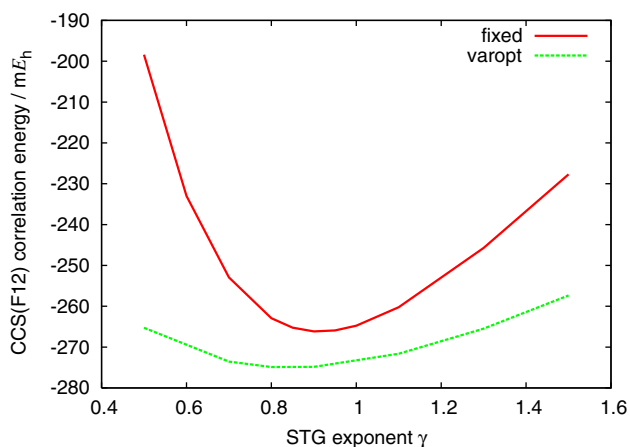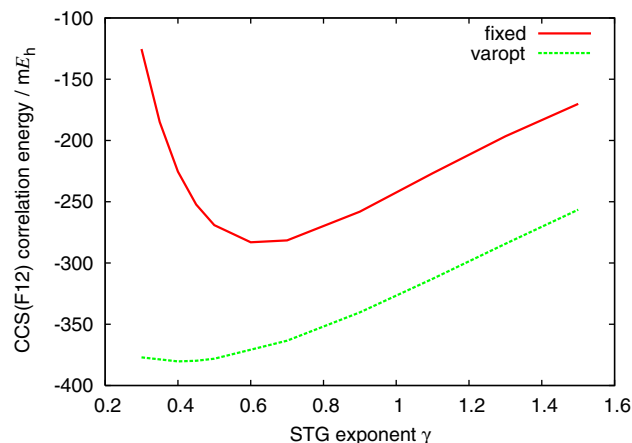

Fig. 2. CCS(F12) aVTZ correlation energies for the C_2 molecule for a wide range of γ in mE_h using the *fixed* and *varopt* approach.

Table 5
Frozen-core *varopt* CCS(F12) aVTZ correlation energies for the HF molecule using different correlation factors. The best result obtained with the STG-6G approach is −275.012 mE_h (compare previous tables).

$f(r_{12})$	γ	
r_{12}	×	−194.510
$e^{-\gamma r_{12}}$	0.2	−232.274
	0.4	−257.499
	0.6	−270.475
	0.8	−274.884
	1.0	−273.670
	1.2	−268.843
	1.4	−261.616
$r_{12}e^{-\gamma r_{12}}$	0.2	−264.958
	0.4	−267.164
	0.6	−205.494
	0.8	−126.788
	1.0	−74.807
	1.2	−54.395
	1.4	−53.573
$r_{12}\mathrm{erfc}(\gamma r_{12})$	0.2	−270.644
	0.4	−131.651
	0.6	−50.914
	0.8	−57.898
	1.0	−89.155
	1.2	−114.661
	1.4	−127.044

The linear correlation factor was introduced to fit the short range around the electron–electron cusp and introduces incorrect medium to long-range behaviour of the wave function. We have also investigated $f(r_{12}) = r_{12}\exp(-\gamma r_{12})$ (RSTG) and $f(r_{12}) = r_{12}\mathrm{erfc}(\gamma r_{12})$ for a range of γ. Neither of these correlation factors improve upon the STG, although similar correlation energies may be obtained if γ is properly optimised. The optimum values of γ for both of these functions are much smaller than that of the STG, which is expected from a comparison of the quadratic and cubic r_{12} terms in the Taylor expansions. In general we may tentatively conclude that the long-range tails of these correlation factors do not improve the description of the correlation in CCS(F12) calculations, but rather worsen it. The Slater-type correlation factor continues to be the best choice of all investigated correlation factors.

5.5. Investigations on reactions

The next step is to investigate energy differences, i.e. reaction energies. Results for the correlation contribution using the fro-

Fig. 1. CCS(F12) aVTZ correlation energies for the HF molecule for a wide range of γ in mE_h using the fixed and varopt approach.

Table 6
Reaction energy contributions for different coupled-cluster methods and basis sets in millihartrees. The CCS(F12) results are obtained using the aVTZ values from Table 4.

Method	ΔCCS(F12)		ΔCC2		
	fixed	varopt	aVDZ	aVTZ	aVQZ
$C_2H_2 + H_2 \rightarrow C_2H_4$	1.17	3.71	12.65	8.50	7.37
$H_2O_2 + H_2 \rightarrow 2H_2O$	0.67	4.20	11.18	5.94	3.99
$CH_4 + 4H_2O_2 \rightarrow CO_2 + 6H_2O$	1.90	15.60	7.31	10.24	8.21

zen-core approximation are shown in Table 6. The CCS(F12) numbers were computed using the frozen-core aVTZ correlation energies from Tables 3 and 4. The Hartree–Fock contributions are not listed but must not be forgotten yielding negative reaction energies in total. In the framework of this study we are only interested in the loss of accuracy when going from CC2 to CCS(F12). Overall the *varopt* results perform very poorly and the *fixed* values are even worse. The CCS(F12) results clearly do not provide a homogenic description of the correlation energy in molecules, in other words the problem is that the CCS(F12) correlation energy amounts 85% of the CC2 limit in the case of CO_2 but 97% in the case of H_2. In this respect the presence of the conventional expansion for the double excitations is a very important component of F12 methods for chemical applications.

6. Summary and conclusions

Almost all of the key components of modern R12 methods can be traced back to Kutzelnigg's breakthrough paper in 1985. Not only did he demonstrate that the rate of convergence to the basis set limit is greatly accelerated if the correlation cusp is satisfied, but he also solved the problem of the numerous, expensive many-electron integrals that arise through use of an approximate resolution of the identity. Moreover, Kutzelnigg found that for helium, the simple wave function $(1 + \frac{1}{2}r_{12})\Phi$ recovered more than 80% of the correlation energy (using the bare nuclear Hamiltonian as the zeroth order operator). In this paper we have revisited Kutzelnigg's simple ansatz, replacing linear r_{12} with the modern Slater-type correlation factor. We have asked the question "How much of the correlation energy is recovered for molecules?" We have therefore performed calculations at the CC2 level of theory, replacing the conventional expansion in virtual orbital pairs with the R12 geminal basis. Even though only occupied Hartree–Fock orbitals are used in the geminal basis, 80–95% of the CC2 basis set limit are obtained. This is astonishingly large, considering that for linear r_{12} only around 60% is recovered. However, the proportion of correlation energy recovered and the exponent γ in the geminal basis vary greatly between the molecules we have investigated. Nonetheless, our results clearly demonstrate the immense redundancy between the conventional and geminal basis functions in explicitly correlated calculations. Furthermore, it also indicates that in GGn methods the geminal expansion should converge rapidly, provided that the strong orthogonality functional is used [27]. We postulate that for the development for future R12 methods it may be possible to capitalise on the redundancy between the geminal and conventional excitations and to construct smaller sets of virtual orbitals, perhaps in the fashion of Almlöfs' dual basis sets [52], as proposed in Refs. [46,53]. On the other hand, the fact that in R12 calculations 80 - 95% of the correlation energy is recovered

by the geminal basis alone clearly explains why it is possible to achieve quintuple-ζ quality with only triple-ζ basis sets.

References

[1] W. Kutzelnigg, Theor. Chim. Acta 68 (1985) 445.
[2] T. Kato, Commun. Pure Appl. Math. 10 (1957) 151.
[3] R.T. Pack, W. Byers Brown, J. Chem. Phys. 45 (1966) 556.
[4] D.P. Tew, J. Chem. Phys. 129 (2008) 014104.
[5] W. Klopper, W. Kutzelnigg, Chem. Phys. Lett. 134 (1987) 17.
[6] W. Klopper, R. Röhse, W. Kutzelnigg, Chem. Phys. Lett. 178 (1991) 455.
[7] W. Klopper, J. Noga, J. Chem. Phys. 103 (1995) 6127.
[8] W. Klopper, C.C.M. Samson, J. Chem. Phys. 116 (2002) 6397.
[9] F.R. Manby, J. Chem. Phys. 119 (2003) 4607.
[10] S. Ten-no, Chem. Phys. Lett. 398 (2004) 56.
[11] D.P. Tew, W. Klopper, C. Neiss, C. Hättig, Phys. Chem. Chem. Phys. 9 (2007) 1921.
[12] D.P. Tew, W. Klopper, C. Hättig, Chem. Phys. Lett. 452 (2008) 326.
[13] T.B. Adler, G. Knizia, H.-J. Werner, J. Chem. Phys. 127 (2007) 221106.
[14] E.F. Valeev, Phys. Chem. Chem. Phys. 10 (2008) 106.
[15] E.F. Valeev, T.D. Crawford, J. Chem. Phys. 128 (2008) 244113.
[16] T. Shiozaki, M. Kamiya, S. Hirata, E.F. Valeev, J. Chem. Phys. 129 (2008) 071101.
[17] J. Noga, S. Kedžuch, J. Šimunek, S. Ten-no, J. Chem. Phys. 128 (2008) 174103.
[18] B.J. Persson, P.R. Taylor, J. Chem. Phys. 105 (1996) 5915.
[19] R. Polly, H.-J. Werner, P. Dahle, P.R. Taylor, J. Chem. Phys. 124 (2006) 234107.
[20] P. Dahle, T. Helgaker, D. Jonsson, P.R. Taylor, Phys. Chem. Chem. Phys. 9 (2007) 3112.
[21] P. Dahle, T. Helgaker, D. Jonsson, P.R. Taylor, Phys. Chem. Chem. Phys. 10 (2008) 3377.
[22] O. Christiansen, H. Koch, P. Jørgensen, Chem. Phys. Lett. 243 (1995) 409.
[23] H. Fliegl, C. Hättig, W. Klopper, J. Chem. Phys. 124 (2006) 44112.
[24] H. Fliegl, W. Klopper, C. Hättig, J. Chem. Phys. 122 (2005) 84107.
[25] T. Helgaker, P. Jørgensen, J. Olsen, Molecular Electronic-Structure Theory, Wiley, Chichester, 2000.
[26] W. Kutzelnigg, W. Klopper, J. Chem. Phys. 94 (1991) 1985.
[27] D.P. Tew, W. Klopper, F.R. Manby, J. Chem. Phys. 127 (2007) 174105.
[28] E.F. Valeev, Chem. Phys. Lett. 395 (2004) 190.
[29] P. Wind, W. Klopper, T. Helgaker, Theor. Chim. Acta 107 (2002) 173.
[30] W. Klopper, F.R. Manby, S. Ten-no, E.F. Valeev, Int. Rev. Phys. Chem. 25 (2006) 427.
[31] A.J. May, F.R. Manby, J. Chem. Phys. 121 (2004) 4479.
[32] A.J. May, E. Valeev, R. Polly, F.R. Manby, Phys. Chem. Chem. Phys. 7 (2005) 2710.
[33] D.P. Tew, W. Klopper, J. Chem. Phys. 123 (2005) 074101.
[34] F.R. Manby, H.-J. Werner, T.B. Adler, A.J. May, J. Chem. Phys. 124 (2006) 094103.
[35] D.P. Tew, W. Klopper, J. Chem. Phys. 125 (2006) 094302.
[36] S. Ten-no, J. Chem. Phys. 126 (2007) 014108.
[37] H.-J. Werner, T.B. Adler, F.R. Manby, J. Chem. Phys. 126 (2007) 164102.
[38] D. Yamaki, H. Koch, S. Ten-no, J. Chem. Phys. 127 (2007) 144104.
[39] O. Marchetti, H.-J. Werner, Phys. Chem. Chem. Phys. 10 (2008) 3400.
[40] G. Knizia, H.-J. Werner, J. Chem. Phys. 128 (2008) 154103.
[41] S. Ten-no, Chem. Phys. Lett. 447 (2007) 175.
[42] W. Klopper, Chem. Phys. Lett. 186 (1991) 583.
[43] S. Ten-no, J. Chem. Phys. 121 (2004) 117.
[44] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[45] R.A. Kendal, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[46] C. Neiss, C. Hättig, W. Klopper, J. Chem. Phys. 125 (2006) 64111.
[47] B.T. Psciuk, V.A. Benderskii, H.B. Schlegel, Theor. Chem. Acc. 118 (2007) 75.
[48] X. Li, J. Paldus, J. Chem. Phys. 110 (1999) 2844.
[49] J.M.L. Martin, T.J. Lee, G.E. Scuseria, P.R. Taylor, J. Chem. Phys. 97 (1992) 6549.
[50] G.E. Scuseria, T.J. Lee, J. Chem. Phys. 93 (1990) 5851.
[51] H.-J. Werner, K. Pflüger, Ann. Rep. Comput. Chem. 2 (2006) 53.
[52] R. Jurgens-Lutovsky, J. Almlöf, Chem. Phys. Lett. 178 (1991) 451.
[53] W. Klopper, J. Noga, H. Koch, T. Helgaker, Theor. Chem. Acc. 97 (1997) 164.